IJE TRANSACTIONS B: Applications Vol. 31, No. 8, (August 2018) 1356-1363

International Journal of Engineering

Journal Homepage: www.ije.ir

CO_2 Selective Carbon Tubular Membrane: The Effect of Stabilization Temperature on BTDA-TDI/MDI P84 co-polyimide

N. Sazali[a,b], W. N. W. Salleh*[a,b], A.F. Ismail[a,b], N. H. Ismail[a,b], M. N. M. Sokri[a,b], N. A. H. M. Nordin[e]

[a] *Advanced Membrane Technology Research Centre (AMTEC), Universiti Teknologi Malaysia, 81310 Skudai, Johor Darul Takzim, Malaysia*
[b] *School of Chemical and Energy Engineering (FCEE), Universiti Teknologi Malaysia, 81310 Skudai, Johor Darul Takzim, Malaysia*
[c] *Fuel Cell Institute (SELFUEL), Universiti Kebangsaan Malaysia, 43600 UKM Bangi, Selangor, Malaysia.*
[d] *School of Chemical Sciences and Food Technology, Faculty of Science and Technology, Universiti Kebangsaan Malaysia, 43600 UKM Bangi, Selangor, Malaysia.*
[e] *Chemical Engineering Department, Universiti Teknologi Petronas (UTP), 32610 Seri Iskandar, Malaysia*

PAPER INFO

Paper history:
Received 11 November 2017
Received in revised form 13 December 2017
Accepted 17 Januray 2018

Keywords:
Gas Permeation
Selectivity
P84 co-polyimide
Tubular Support
Carbon Membrane

ABSTRACT

Membranes offer remarkable attributes such as possessing small equipment footprints, having high efficiency and are environmentally friendly, with carbon membranes progressively investigated for gas separation applications. In this study, carbon tubular membranes for CO_2 separation are prepared via dip-coating method with P84 co-polyimide as carbon precursor. The prepared membranes were characterized using Thermogravimetric Analysis (TGA), pore structure analysis Brunauer-Emmett-Teller (BET), Fourier Transform Infrared Spectroscopy (FTIR) and pure gas permeation system. The permeation properties of the carbon membranes are measured and analyzed using CO_2, CH_4 and N_2 gases. The P84-based carbon tubular membrane stabilized at 300°C and featured excellent permeation properties with permeance range of 2.97±2.18, 3.12±4.32 and 206.09±3.24 GPU for CH_4, N_2 and CO_2 gases, respectively. This membrane exhibited the highest CO_2/CH_4 and CO_2/N_2 selectivity of 69.48±1.83 and 65.97±2.87, respectively.

***doi**: 10.5829/ije.2018.31.08b.26*

Greek Symbols

μ	Micro (0.000001)
γ	Gamma
$(P/l)_i = \frac{Q_i}{\Delta p.A} = \frac{Q}{\pi D l \Delta P}$	Permeance,P
$\alpha_{A/B} = \frac{P_A}{P_B} = \frac{(P/l)_A}{(P/l)_B}$	Selectivity, α

1. INTRODUCTION

Nowadays, gas separation is one of the premier applications of membrane technology. The improvement of gas separation membranes in past years have accelerated for gas refining applications, especially natural gas [1,2]. For the past 30 years, membrane technology has been prominently used as a method to obtain various types of gases with high purity. In order to attain membranes that exhibit high selectivity, high permeability, high chemical and thermal steadiness, membranes are developed using polymeric materials [3]. Nevertheless, it also believed the reduction in polymeric membrane effectiveness with time can be affected by fouling, compaction, chemical degradation and thermal instability [4]. Because of the limited thermal stability and lack of resistance towards abrasions and chemical attacks, polymeric membranes encountered a drawback when applied in separation processes where hot reactive gases are present [5]. This has brought about a movement

*Corresponding Author Email: *hayati@petroleum.utm.my* (W. N. W. Salleh)

Please cite this article as: N. Sazali, W. N. W. Salleh, A.F. Ismail, N. H. Ismail, M. N. M. Sokri, N. A. H. M. Nordin, CO_2 Selective Carbon Tubular Membrane: The Effect of Stabilization Temperature on BTDA-TDI/MDI P84 co-polyimide, International Journal of Engineering (IJE), IJE TRANSACTIONS B: Applications Vol. 31, No. 8, (August 2018) 1356-1363

to explore inorganic membranes to separate gas mixtures [6]. Carbon membrane provides better permeability and selectivity over polymeric membrane, while being able to withstand harsh environmental conditions (high temperature, etc.) [7,8].

Recently, researchers have developed an interest in using various kinds of polymeric materials such as polyimides for carbon membrane precursor [4,9]. P84 co-polyimide can withstand temperatures of more than 300°C without losing its shape; because it does not undergo a melting phase transition [10,11]. Mangindaan et al. [12] reported that the new development of polyimide P84 co-polyimide blended with TAEA cross-linked membranes have exhibited good separation performance for acetone dehydration. Furthermore, Choi et al. [13] had investigated the chemical cross-linked asymmetric P84 co-polyimide hollow fibre membranes using the dry-wet spinning process. The results showed an enhancement in the separation performance, as well as, in the gas transport properties of the fabricated membranes. Regarding the membrane thickness, Ren et al. [11] had investigated the thickness on the formation of asymmetrical flat sheet membranes prepared with P84 (BTDA-TDI/MDI co-polyimide)/N-methyl-2-pyrrolidone (NMP)/GBL (γ-butyrolactone) casting solutions. The results showed that high flux and a large MWCO were exhibited by membranes fabricated via the wet spinning process [11]. Previous researchers have prepared asymmetrical membranes based on P84 co-polyimide by the phase inversion technique. The asymmetrical membrane prepared from acetone/NMP/P84 chemical mixture exhibited the best gas separation performance with a permeance of 17, 1.8, 0.82 and 0.092 GPU for He, CO_2, O_2 and N_2, respectively; along with a selectivity of 200, 20 and 9 for He/N_2, CO_2/N_2 and O_2/N_2, respectively [14]. It is believed that the development of a carbon membrane from excellent polymer precursor would significantly improved the final membrane properties. Therefore, P84 co-polyimide was selected to be used in this study.

Carbon membranes are more suitable for gas separation processes at high temperatures between 500-900°C [15,16]. Further studies regarding the stabilization condition by using polyimides as a precursor membrane are promising since they offer greater stability among other materials [17]. During the stabilization process, a chemical reaction is initiated during the isothermal step, and it was suggested that the majority of nitriles take part in the cyclisation and trimerisation reactions below 400°C [18]. Cipriani et al. [18] performed carbonization on a thin film polyacrylonitrile (PAN) at a stabilization temperature below 400°C where the final structure of the samples resembled graphitised structures. Barbosa-Coutinho et al. [19] had indicated that at the stabilization temperature of above 500°C, an intensive degradation of the polyetherimide-based carbon membrane was observed. This is because the extent of membrane exposure under maximum temperature of stabilization was decisive in the final membrane morphologic characteristics and properties [19]. Furthermore, Hameed et al. [20] had investigated the effect of oxidative stabilization and carbonization processes on the structure, mass and mechanical properties of polyacrylonitrile (PAN) precursor fibres. The results revealed that after stabilization at a maximum temperature of 255°C and carbonization at a maximum temperature of 800°C, the tensile strength and modulus of the fibres had increased.

Different precursors would require different stabilization conditions due to the chemical structure and thermal behaviour of those particular precursor materials. Despite their impact on carbon membrane properties, researches specifically on the stabilization conditions are very limited in the current literature since most researches focusing on carbonization or pyrolysis conditions. Therefore, this work aims to investigate the effect of the stabilization temperature on CO_2 separation of the prepared carbon membrane. Furthermore, majority of gas separation membranes are framed into support membranes for higher mechanical steadiness as compared to unsupported carbon membranes [21]. Considering that supported carbon membranes exhibited superior gas permeation properties, supported carbon tubular membranes was utilised in this study [22,23]. Based on the author's knowledge, the effects of stabilization temperatures on P84-based carbon membranes have not been reported in the current literature. The investigation was conducted by performing the stabilization process at various temperatures (250, 300, 350, 400 and 450°C) with constant heating rate of 2°C/min under N_2 atmosphere, and a flow rate of 200 ml/min. The characterization methods employed were thermogravimetric analysis (TGA), Fourier transform infrared spectroscopy (FTIR) and Brunauer–Emmett–Teller (BET). It is expected that the findings from this study would help bridge the literature gap in the understanding of the influence of stabilization temperature for the improvement of gas separation properties.

2. EXPERIMENTAL

2. 1. Materials Commercially available co-polyimide BTDA-TDI/MDI (P-84) procured from Sigma Aldrich (CAS#: 58698-66-1) was chosen as a precursor for the fabrication of carbon-based membranes. The measured density of P84 co-polyimide was 1.31g/cm^3. Additionally, the glass transition temperature (Tg) of this polymer was 315°C [14]. N-Methyl-2-Pyrrolidone was purchased from Merck (Darmstadt, Germany) and employed as a solvent in the preparation of the dope

solution. Porous tubular ceramic, TiO_2 (4.5-5.5mm), with a coating of ZrO_2 (2-3nm) on the inner surface was purchased from Shanghai Gongtao Ceramics Co., Ltd (China). The dimensions of the porous tubular ceramic were 8cm in length, 13mm for the outer diameter and 10mm for the inner diameter. The porosity of the support was 40-50% with an average pore size of 0.2µm. All chemicals were utilised without further modification.

2. 2. Carbon Membrane Preparation The supported carbon membranes were prepared via dip-coating of the tubular support into a dope solution consisting of 15wt% of P84 co-polyimide and 85wt% of NMP over the external surface of the tubular support. This composition was obtained based on our previous study [24, 25]. The ceramic support was dipped into the dope solution for 15 minutes. The membrane was then dried in the oven at 80°C for 24 hours. Next, the membranes were immersed in methanol for 2 hours, followed by drying at 100°C for 24 hours to allow slow removal of the solvent. The dip-coating cycles were repeated three times to eliminate possible pinhole presences on the surface of the prepared carbon tubular membranes. The dried supported precursor membranes were then placed inside a Carbolite horizontal tubular furnace for stabilization and carbonization processes. In this study, two steps of the heat treatment were involved. In the first step, the membranes were treated at different stabilization temperatures (250, 300, 350, 400 and 450°C) with a heating rate of 2°C/min under N_2 atmosphere (200ml/min). In the second step, the membranes were carbonized up to 800°C at the same heating rate and gas flow as mentioned in step 1. The nomenclature of the resultant carbon membranes was given in the form of (CM-stabilization temperature);CM-250/CM-300/CM-350/CM-400/CM-450. Carbon membranes without substrate were also prepared via similar procedure for characterization purposes.

2. 3. Membrane Characterization Several characterization methods were used to study the carbon membranes fabricated at different stabilization temperatures. The weight loss of carbon membranes during the heat treatment process was characterised using thermogravimetric analysis (TGA 2050). The analysis was carried out with a ramp of 10°C/min with temperature ranging from 50°C to 800°C. The purge gas was N_2 and its flow rate was controlled at 20ml/min. A small piece of the tested membranes was cut and conditioned in liquid nitrogen to leave an unreformed structure to be mounted on sample stubs. The samples were then sputter coated with gold under a vacuum. Fourier Transform Infrared Spectroscopy (FTIR) and Single Reflection Diamond for the Spectrum Two (PerkinElmer, L1600107) were used to distinguish the actuality of the functional groups in a membrane. The FTIR sequences displayed the variation of the functional groups in the membranes once heated from room temperature to carbonization temperature. The apparent surface area of the carbon membrane particles was calculated using Brunauer–Emmett–Teller (BET) equation (Micromeritics ASAP 2010) obtained from the equipment software. The sample was heated at 130°C for 1 h to remove any trapped moisture.

Permeance, P:
$$(P/l)_i = \frac{Q_i}{\Delta p.A} = \frac{Q}{\pi D l \Delta P} \quad (1)$$

Selectivity, *α*:
$$\alpha_{A/B} = \frac{P_A}{P_B} = \frac{(P/l)_A}{(P/l)_B} \quad (2)$$

where P/l is the permeance of the membrane, Qi is the volumetric flow rate of gas i at standard temperature and pressure (cm^3 (STP/s), p is the pressure difference between the feed side and the permeation side of the membrane (cmHg), A is the membrane surface area (cm^2), D is the outer diameter of the membrane (cm) and l is the effective length of the membrane (cm). The permeate volumetric flow rate was measured by the soap bubble flow meter reading of 1.0ml. This permeation test was repeated with two other different membrane samples. The gas permeation test was conducted at ambient temperatures. Similar gas permeation was also used in previous studies [24,25].

3. RESULTS AND DISCUSSION

3. 1. Thermal Behaviour Analysis The weight loss of P84-based polymeric membranes during the carbonization process was assessed by TGA by measuring the changes in the physical and chemical properties of the membranes as a function of increasing temperatures. Figure 1 illustrated the weight variation of polymers during the heating process, from 50°C to 800°C. As seen in Figure 1, P84- based polymeric membranes exhibited two distinct weight loss patterns. The first degradation of precursor membrane from its original weight to 94% started at approximately 40°C to 460°C, which was due to moisture evaporation. The second stage of precursor membrane degradation began at temperature range of 460°C to 800°C, which represented the degradation temperature of P84 co-polyimide. According to the TGA thermogram obtained, the degradation temperature (Td), which was defined as the temperature corresponding to 5-10% weight loss of the precursor, was observed at 470°C. This explained the high thermal resistance exhibited by P84 co-polyimide. Studies have found that stabilization between the temperature range of glass transition temperature, Tg, and degradation temperature, Td, can effectively prevent melting during carbonization of thermal plastic

polymers, such as polyimides (PI) [26]. The glass transition temperature of P84 co-polyimide, as reported in previous research, was 315°C [11]. Therefore, in this study, stabilization temperatures in the range of 250°C-450°C were investigated.

3. 2. Fourier Transform Infrared Spectroscopy (FTIR) Molecular orientation analysis of P84-based carbon membranes under various stabilization temperatures was performed using FTIR; as illustrated in Figure 2. The chemical structural changes that took place through the transformation of polymer to carbon were observed. The results indicated that the intensity of the prepared carbon membranes decreased compared to the prepared precursor membranes. The most significant difference was found at a lower wave number, from 400 to 1900cm^{-1}. The peak at 3442cm^{-1} was attributed to the O-H stretching vibration of the OH functional group. The intensity of this peak was reduced due to the evaporation of water molecules at higher stabilization temperatures.

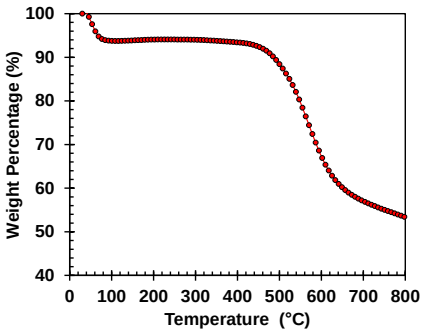

Figure 1. TGA profile of P84-based polymeric membrane

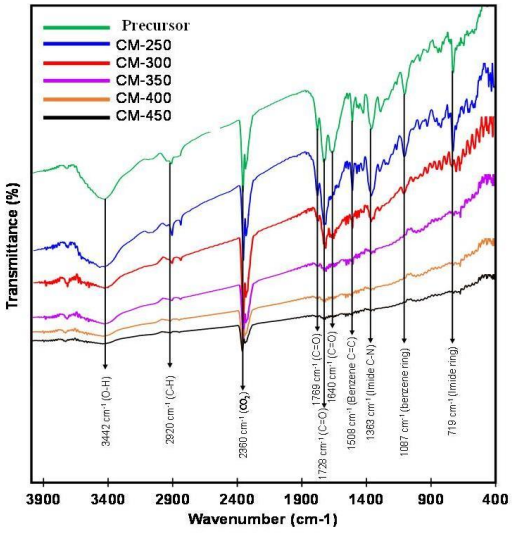

Figure 2. Molecular orientation analysis of precursor and carbon membrane prepared at different stabilization temperature.

The absorption peak at 2920cm^{-1} corresponded to the symmetric and asymmetric stretching vibrations of CH_2 groups [27]. The doublet at 2360cm^{-1} was due to atmospheric CO_2. The absorption peak at 1769, 1728 and 1640cm^{-1} was associated to symmetric C=O stretching and asymmetric C=O stretching of imide [28, 29]. The peaks at 1508cm^{-1} and 1087cm^{-1} were attributed to the symmetric stretching vibrations of C-C groups in the benzene rings. In addition, the stretching of C–N in the imide group can be found at 1363cm^{-1}. The aforementioned absorption peaks' intensity significantly reduced with the increment of stabilization temperatures, from 250°C to 350°C. This phenomenon indicated that the demolition of P84-based polymeric membrane structure prior to the formation of P84-based carbon membrane was at a higher stabilization temperature, followed by carbonization temperature at 800°C.

Based on TGA analysis, it can be observed that P84-based polymeric membranes undergone thermal degradation during the heat treatment process. Upon carbonization, precursor membranes may degrade via a number of mechanisms including random scission, cross-linking and side group elimination [30]. The existence of free radicals along the backbone of a polymer or any other locations on the chain could result in random scission. Cross-linking generally resulted after stripping of some substituent, and involves the creation of bonds between two adjacent polymer chains [31]. These processes are very important during char's formation as higher molecular weight structures that are less easily volatilised are generated. During chain elimination reaction, the bonds connecting the side groups of polymer chain to the chain itself were broken giving products which are small enough to be volatilised. Specifically, the weight loss of the precursor membranes after the carbonization process were attributed to the release of ammonia (NH_3), hydrogen cyanide (HCN), methane (CH_4), hydrogen (H_2), nitrogen (N_2), oxygen (O_2), carbon monoxide (CO), carbon dioxide (CO_2), benzene, phthalimide and others [32]. As mentioned previously, cross-linking occurs more dominantly compared to scission reaction in P84-based polymeric membranes due to their thermal stability in which greater cross-linking density will give rise to higher Tg. As temperature increased above Tg, the polymer packing density increases [33].

3. 3. Pore Structure Analysis The surface area and pore volume of porous materials were observed from the isotherm adsorptions where it was measured at -196°C, with a relative pressure of around 0.03 due to the molecular size of the N_2, along with low running temperature. Total pore volume and the volume of the micropores were estimated from the absorption measurements where they were automatically analyzed by the instrument software. Generally, porous materials

are characterised in terms of pore size derived from gas sorption data and IUPAC conventions; this was proposed in order to classify pore sizes and gas sorption that reflect the relationship between porosity and sorption [34]. Figure 3 presented the N_2 adsorption isotherms for the carbon membrane prepared at different stabilization temperatures. The N_2 adsorption result displayed the characteristics of Type III isotherm. Membranes with a high possibility of microporous materials have low adsorption energy [33]. Initially, at a relative pressure of 0 to 0.9, the increment of nitrogen volume was slow and this was consistent for all stabilization temperatures. However, from 0.9 to 1, each stabilization temperature exhibited a different value where all of them made an abrupt increase in the high pressure region. This type of isotherm illustrated the existence of the multi-layered formation [35]. It was also revealed that there was no flattish portion in the curve which indicated that monolayer formation was missing from the carbon membrane sample (Mangindaan *et al.*, 2014). The result for N_2 absorption obtained for this study can be considered as low in value, and all the samples had a similar trend of results. It was observed that the higher N_2 uptake was exhibited for CM-300 in comparison to other stabilization temperatures applied.

Table 1 demonstrated the effect of stabilization temperatures on the membrane pore structure. It was observed that when the stabilization temperature was increased from 250°C to 450°C, the pore size average radius decreased. This occurred because rigid chains tend to shrink and stress, which results in smaller pore size with the increment of stabilization temperature [36]. The lowest surface area was exhibited by the carbon membrane prepared at 300°C.

It was reported that the reduction in BET surface area may be due to the deterioration of the original polymer backbone and the increment in the formation of activated points composed of oxygen-containing groups during the stabilization process; this affects the developed pore system of the carbon membrane produced [21].

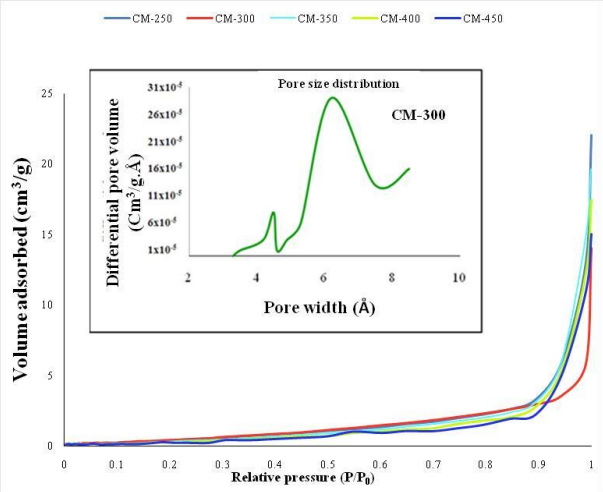

Figure 3. N_2 adsorption isotherms of P84-based carbon membranes

According to previous studies, the optimum pore size range for carbon membrane is between 3 to 5Å [10]. In this study, the pore size range obtained ranged between 3 to 10Å which showed that the pore size of the carbon membranes was still in range with the gas molecular size. The pore size range (Å) was measured using the standard Barrett-Joyner-Halenda (BJH) analysis that refers to the pore size distribution determination method [37]. Previous researchers suggested that the amount of ultra micropores (< ~7Å) must exceed the amount of the micropores (> ~7Å) in order to obtain high results in gas separation performance [25].

3. 4. Gas Permeation Measurements The gas permeation properties of the prepared precursor and carbon membranes were measured using the gas permeation test apparatus at room temperature. The permeance of three pure gases with different molecular sizes, CO_2 (3.30Å), N_2 (3.64Å) and CH_4 (3.80Å), through the resulted precursor and carbon membranes prepared at different stabilization temperatures were measured and shown in Table 2. The results revealed that stabilization parameters can essentially influence the execution of the subsequent carbon membrane performance. It can be indicated that carbon membranes provide excellent performance compared to the precursor membranes in terms of gas permeation and selectivity. This was due to the arrangement of pore structure by cross-linking and volatilisation of minor vaporous particles delivered by thermal degradation during stabilization. Carbon membrane, which was stabilized at 300°C, showed superior selectivity. This was because its pore system consists of extensive openings with narrow constriction [38]. The results demonstrated that gas permeance of the prepared membranes follow the order of $CO_2 > N_2 > CH_4$, which are in accordance to their kinetic diameters [39]. These findings are in agreement with work accomplished in previous studies [36].

TABLE 1. Effect of stabilization temperature on the membrane pore structure

Stabilization Temperature (°C)	BET surface area (m^2/g)	Total pore volume (cm^3/g)	Micropore volume (cm^3/g)
CM- 250	2.8176	0.0248	0.0017
CM-300	2.2875	0.0276	0.0015
CM-350	2.7419	0.0197	0.0011
CM-400	2.5854	0.0157	0.0013
CM-450	2.3111	0.0118	0.0010

TABLE 2. Gas permeation properties of P84-based polymeric and carbon membranes

Membrane	Permeability			Selectivity	
	CH_4	N_2	CO_2	CO_2/CH_4	CO_2/N_2
Precursor	0.76 ± 4.57	0.78 ± 5.23	2.01 ± 6.32	2.64 ± 1.76	2.59 ± 2.33
CM-250	2.73 ±5 .32	2.90 ± 4.98	174.40 ± 5.21	63.96 ± 2.53	60.15 ± 2.76
CM-300	2.97 ± 4.49	3.12 ± 5.13	206.09 ± 5.78	69.48 ± 1.83	65.97 ± 2.87
CM-350	2.86 ± 5.76	3.02 ± 6.22	183.81 ± 4.51	64.22 ± 2.64	60.90 ± 3.01
CM-400	2.64 ± 22	2.76 ± 18	164.66 ± 4.23	62.37 ± 5.19	59.66 ± 5.72
CM-450	2.58 ± 19	2.74 ± 61	158.77 ± 3.54	61.54 ± 3.76	57.96 ± 1.22

In addition, as the stabilization temperature was increased, the degree of deterioration and cross-linking in the membrane increased, which resulted in different micropore structures of carbon membranes; as evident via the N_2 adsorption analysis. Thus, controlling the stabilization temperature can be used as a means to fine-tune the gas separation properties of the derived carbon membranes. It is believed that the stabilization processes offer the potential to prevent melting and fusion of polymeric membranes and avoid excessive volatilisation of carbon elements in the following carbonization process. As a result, the final carbon yielded from the precursor can be maximised; as reported in previous studies [7]. Numerous researchers have noted that the microstructure of carbon membranes (pore size, pore volume and pore distribution) could be customised by controlling the states of the heat treatment process.

4. CONCLUSION

Carbon tubular membranes were successfully prepared by heat treatment with the use of commercially available P84 co-polyimide. Carbon membranes were stabilized at different stabilization temperatures before carbonized at 800°C. The stabilization temperatures have prominent effect on the membrane properties especially their pore structure, and ultimately their gas separation properties. The carbon membrane stabilized at 300°C possessed greater permeation properties with CO_2 permeability of 206.09±3.24 GPU, and with the selectivity of 69.48±1.83 and 65.97±2.87 for CO_2/CH_4 and CO_2/N_2, respectively. The gas permeation properties of the carbon membranes were markedly increased in magnitude compared to the polymeric precursor membranes. This was due to the formation of pore structures by cross-linking and volatilisation of small gaseous molecules produced by minor thermal degradation during stabilization. The overall results demonstrated that the P84-based carbon membrane is a promising material for CO_2/CH_4 and CO_2/N_2 separation.

5. ACKNOWLEDGEMENT

The authors gratefully acknowledge the financial support from Ministry of Higher Education and Universiti Teknologi Malaysia (UTM) under Higher Institution Centre of Excellence Scheme (Project Number: R. J090301.7846.4J188) and acknowledge technical and management support from Research Management Centre (RMC), Universiti Teknologi Malaysia. Author would also like to thanks to Professor Yuji Iwamoto and Professor Sawao Honda from Department of Frontier Materials, Graduate School of Engineering, Nagoya Institute of Technology, Japan for their contribution in laboratory equipment.

6. REFERENCES

1. Adewole, J. K., Ahmad, A. L., Ismail, S. and Leo, C. P. "Current challenges in membrane separation of CO_2 from natural gas: A review", ***International Journal of Greenhouse Gas Control***, Vol. 17, (2013), 46-65.
2. Zhang, Y., Sunarso, J., Liu, S. and Wang, R. "Current status and development of membranes for CO_2/CH_4 separation: A review", ***International Journal of Greenhouse Gas Control***, Vol. 12, (2013), 84-107.
3. Sridhar, S., Smitha, B. and Aminabhavi, T. M. "Separation of Carbon Dioxide from Natural Gas Mixtures through Polymeric Membranes—A Review". ***Separation & Purification Review***, Vol. 36, (2007), 113-174.
4. Xiao, Y., Low, B. T., Hosseini, S. S., Chung, T. S. and Paul, D. R. "The strategies of molecular architecture and modification of polyimide-based membranes for CO_2 removal from natural gas—A review", ***Progress in Polymer Science***, Vol. 34, (2009), 561-580.
5. Saufi, S. M. and Ismail, A. F., "Fabrication of carbon membranes for gas separation—A review", ***Carbon***, Vol. 42, (2004), 241-259.
6. Peng, N., Widjojo, N., Sukitpaneenit, P., Teoh, M. M., Lipscomb, G. G., Chung, T.-S. and Lai, J.-Y. "Evolution of polymeric hollow fibers as sustainable technologies: Past, present, and future". ***Progress in Polymer Science***, Vol. 37, (2012), 1401-1424.
7. Wan Salleh, W. N., and Ismail, A. F., "Effect of stabilization temperature on gas permeation properties of carbon hollow fiber membrane". ***Journal Applied Polymer Science***, Vol. 127, (2013), 2840-2846.
8. Mahdyarfar, M., Mohammadi, T. and Mohajeri, A., "Gas separation performance of carbon materials produced from phenolic resin: Effects of carbonization temperature and ozone post treatment". ***New Carbon materials***, Vol. 28, (2013), 39-46.
9. Chua, M. L., Xiao, Y. C. and Chung, T.-S., "Modifying the molecular structure and gas separation performance of thermally labile polyimide-based membranes for enhanced natural gas purification". ***Chemical Engineering Science***, Vol. 104, (2013), 1056-1064.

10. Xing, D. Y., Chan, S. Y. and Chung, T.-S., "Fabrication of porous and interconnected PBI/P84 ultrafiltration membranes using [EMIM]OAc as the green solvent". ***Chemical Engineering Science***, Vol. 87, (2013), 194-203.

11. Ren, J. and Li, Z., "Development of asymmetric BTDA-TDI/MDI (P84) copolyimide flat sheet and hollow fiber membranes for ultrafiltration: Morphology transition and membrane performance". ***Desalination***, Vol. (2012), 285, 336-344.

12. Mangindaan, D. W., Woon, N. M., Shi, G. M. and Chung, T. S. "P84 polyimide membranes modified by a tripodal amine for enhanced pervaporation dehydration of acetone". ***Chemical Engineering Science***, Vol. 122, (2015), 14-23.

13. Choi, S.-H., Jansen, J. C., Tasselli, F., Barbieri, G. and Drioli, E. "In-line formation of chemically cross-linked P84® co-polyimide hollow fibre membranes for H_2/CO_2 separation". ***Separation and Purification Technology***, Vol. 76, (2010), 132-139.

14. Lua, A. C. and Shen, Y. "Preparation and characterization of asymmetric membranes based on nonsolvent/NMP/P84 for gas separation", ***Journal of Membrane Science***, Vol. 429, (2013), 155-167.

15. Ismail, A. F. and David, L. I. B. "A review on the latest development of carbon membranes for gas separation". ***Journal of Membrane Science***, Vol.193, (2001), 1-18.

16. Li, L., Qi, W.-B., Wang, H., Zhang, P.-P., Sun, M.-Y., Wang, T.-H., Li, J.-X. and Cao, Y.-M. "Pyrolysis of polyimide membranes from the same dianhydride monomer and different diamines to form carbon membranes". Carbon, Vol. 98,(2016), 735. DOI: 10.1016/j.carbon.2015.10.036

17. Salleh, W. N. W. and Ismail, A. F. "Effect of Stabilization Condition on PEI/PVP-Based Carbon Hollow Fiber Membranes Properties". ***Separation and Science Technology***, Vol. 48, (2013), 1030-1039.

18. Cipriani, E., Zanetti, M., Bracco, P., Brunella, V., Luda, M. P. and Costa, L. "Crosslinking and carbonization processes in PAN films and nanofibers". ***Polymer Degradation and Stability***, Vol. 123,(2016), 178-188.

19. Barbosa-Coutinho, E., Salim, V. M. M. anand Piacsek Borges, C.,"Preparation of carbon hollow fiber membranes by pyrolysis of polyetherimide". ***Carbon***, Vol. 41, (2003), 1707-1714.

20. Hameed, N., Sharp, J., Nunna, S., Creighton, C., Magniez, K., Jyotishkumar, P., Salim, N. V. and Fox, B., "Structural transformation of polyacrylonitrile fibers during stabilization and low temperature carbonization". ***Polymer Degradation and Stability***, Vol. 128, (2016), 39-45.

21. Wang, C., Yu, J., Hu, X.-J. and Huang, Y.,"A review of the development of porous substrate-supported carbon membranes". Carbon, Vol. 85, (2015), 445. DOI: 10.1016/j.carbon.2014.12.072

22. Vinoth Kumar, R., Kumar Ghoshal, A. and Pugazhenthi, G. "Elaboration of novel tubular ceramic membrane from inexpensive raw materials by extrusion method and its performance in microfiltration of synthetic oily wastewater treatment", ***Journal of Membrane Science***, Vol. 490, (2015), 92-102.

23. Mahdyarfar, M., Mohammadi, T. and Mohajeri, A. "Defect formation and prevention during the preparation of supported carbon membranes". ***New Carbon materials***, Vol. 28, (2013), 369-377.

24. Sazali, N., Salleh, W. N. W., Md Nordin, N. A. H., Harun, Z.and Ismail, A. F. "Matrimid-based carbon tubular membranes: The effect of the polymer composition". ***Journal of Applied Polymer Science***, Vol. 132, (2015), 1345. DOI: 10.1002/app.42394

25. Sazali, N., Salleh, W. N. W., Nordin, N. A. H. M. and Ismail, A. F. Matrimid-based carbon tubular membrane: Effect of carbonization environment. ***Journal of Industrial Engineering Chemistry***, Vol. 32, (2015), 167-171.

26. Lin, H. and Yavari, M. "Upper bound of polymeric membranes for mixed-gas CO_2/CH_4 separations. ***Journal of Membrane Science.***, Vol. 475, (2015), 101-109.

27. Matteucci, S., Kusuma, V. A., Sanders, D., Swinnea, S. and Freeman, B. D. "Gas transport in TiO2 nanoparticle-filled poly(1-trimethylsilyl-1-propyne", ***Journal of Membrane Science.***, Vol. 307, (2008), 196-217.

28. Mangindaan, D. W., Min Shi, G. and Chung, T.-S. "Pervaporation dehydration of acetone using P84 co-polyimide flat sheet membranes modified by vapor phase crosslinking". ***Journal of Membrane Science.***, Vol. 458, (2014), 76-85.

29. Shen, Y. and Lua, A. C. "Structural and transport properties of BTDA-TDI/MDI co-polyimide (P84)–silica nanocomposite membranes for gas separation". ***Chemical Engineering Journal***, Vol. 188, (2012), 199-209.

30. Hosseini, S. S. and Chung, T. S. "Carbon membranes from blends of PBI and polyimides for N_2/CH_4 and CO_2/CH_4 separation and hydrogen purification". ***Journal of Membrane Science.***, Vol. 328, (2009), 174-185.

31. Yang, Q., Chung, T.-S., Xiao, Y. and Wang, K. "The development of chemically modified P84 Co-polyimide membranes as supported liquid membrane matrix for Cu(II) removal with prolonged stability". ***Chemical Engineering Science***, Vol. 62, (2007), 1721-1729.

32. Fuertes, A. B. & Centeno, T. A. "Preparation of supported carbon molecular sieve membranes". Carbon, Vol. 37, (1999), 679-684.

33. Alghunaimi, F., Ghanem, B., Alaslai, N., Swaidan, R., Litwiller, E. & Pinnau, I. "Gas permeation and physical aging properties of iptycene diamine-based microporous polyimides". ***Journal of Membrane Science***, Vol. Vol. 490, (2015), 321-327.

34. Zhang, Y.-G. and Lu, M.-C. "Effect of impregnation on the pore structure of a tubular carbon membrane". ***New carbon materials***, Vol. 25, (2010), 475-478.

35. Weng, T.-H., Tseng, H.-H. and Wey, M.-Y. "Fabrication and characterization of poly(phenylene oxide)/SBA-15/carbon molecule sieve multilayer mixed matrix membrane for gas separation". ***International Journal of Hydrogen Energy***, Vol. 35, (2010), 6971-6983.

36. Zhang, K. and Way, J. D. "Optimizing the synthesis of composite polyvinylidene dichloride-based selective surface flow carbon membranes for gas separation". ***Journal of Membrane Science.***, Vol. 369, (2011), 243-249.

37. Villarroel-Rocha, J., Barrera, D. and Sapag, K. "Introducing a self-consistent test and the corresponding modification in the Barrett, Joyner and Halenda method for pore-size determination", ***Micropores and Mesopores Materials***, Vol. 200, (2014), 68-78.

38. Close, J. J., Farmer, K., Moganty, S. S. and Baltus, R. E. "CO_2/N_2 separations using nanoporous alumina-supported ionic liquid membranes: Effect of the support on separation performance". ***Journal of membrane Science***, Vol. 390–391, (2012), 201-210.

39. Shao, P. and Huang, R. Y. M. "Polymeric membrane pervaporation". ***Journal of Membrane Science***, Vol.287, (2007) 162-179.

CO_2 Selective Carbon Tubular Membrane: The Effect of Stabilization Temperature on BTDA-TDI/MDI P84 co-polyimide

N. Sazali[a,b], W. N. W. Salleh[a,b], A.F. Ismail[a,b], N. H. Ismail[a,b], M. N. M. Sokri[a,b], N. A. H. M. Nordin[e]

[a] *Advanced Membrane Technology Research Centre (AMTEC), Universiti Teknologi Malaysia, 81310 Skudai, Johor Darul Takzim, Malaysia*
[b] *School of Chemical and Energy Engineering (FCEE), Universiti Teknologi Malaysia, 81310 Skudai, Johor Darul Takzim, Malaysia*
[c] *Fuel Cell Institute (SELFUEL), Universiti Kebangsaan Malaysia, 43600 UKM Bangi, Selangor, Malaysia.*
[d] *School of Chemical Sciences and Food Technology, Faculty of Science and Technology, Universiti Kebangsaan Malaysia, 43600 UKM Bangi, Selangor, Malaysia.*
[e] *Chemical Engineering Department, Universiti Teknologi Petronas (UTP), 32610 Seri Iskandar, Malaysia*

P A P E R I N F O

Paper history:
Received 11 November 2017
Received in revised form 13 December 2017
Accepted 17 Januray 2018

Keywords:
Gas Permeation
Selectivity
P84 co-polyimide
Tubular Support
Carbon Membrane

چکیده

غشا پیشنهاد مناسبی برای فرایندهایی که دستگاه و تجهیزات کوچکی و بازدهی بالایی هستندو با محیط زیست سازگارند می باشند. با کربنی پیشرفت قابل ملاحظه ای در جداسازی گازها صورت گرفته است. در این تحقیق غشای کربنی لوله ای شکل بروش لایه گذاری با پی-84 و بکمک کو پلی امید بعنوان پیش درآمد برای جداسازی گاز کربنیک تهیه گردیدغشای تهیه شده بروش طیف سنجی و آنالیز ترموگراومتری و انالیزهای ساختاری سطح با خلل و فورج تعیین مشخصات گردید.پایداری و مختصات نفوذ پذیری عالی غشا برای غشا کربنی لوله ای و آنالیز گازهای کربنیک، متان، و نیتروژن به ترتیب در محدوده 2.97±2.18, 3.12±4.32 and 206.09±3.24 GPU و در دمای 300 سانتیگراد CH_4, N_2 و CO_2، می باشند. چنین غشایی نمایش مناسبی از گزینش پذیر ی گازهای CO_2/CH_4 و CO_2/N_2 به ترتیب 69.48±1.83 و 65.97±2.87 می باشند.

***doi**: 10.5829/ije.2018.31.08b.26*